



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C11D 3/50, 3/22, 17/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/55819</b> <b>(43) International Publication Date:</b> 4 November 1999 (04.11.99)
<b>(21) International Application Number:</b> PCT/IB99/00687 <b>(22) International Filing Date:</b> 16 April 1999 (16.04.99) <b>(30) Priority Data:</b> 60/082,725      23 April 1998 (23.04.98)      US <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VELAZQUEZ, Jose Maria [MX/MX]; Monte Chimborazo No. 537, Depto. 201, Colonia Lomas de Chapultepec, Mexico, D.F. (MX). MAR-MOLEJO-RIVAS, Gabriela [MX/MX]; Avenida Centenario 2699 casa 25A, Colonia El Rincon de Centenario, Mexico, D.F. 05190 (MX). RIOSDIAZ, Rudolfo Gilberto [MX/MX]; Sur 107#423 Col Heroes de Churubusco, Mexico, D.F. 09090 (MX). ALVAREZ, Aide Beltran [MX/MX]; 2a. Cda. Vte. Guerrero, Lote 15 Mz 12, Amp. Isidro Fabela, Mexico, D.F. 14030 (MX). MARIN-CARRILLO, Edgar, Manuel [VE/MX]; Paseo de Laureles 404, Dpto. 103, Colonia Bosques de Las Lomas, Mexico, D.F. 11700 (MX). GLOGOWSKI, Mark, William [US/MX]; Cuyamoloya #28, Ha-		cienda de Vallescondido, Atizapan de Zaragoza, Mexico, D.F. 52937 (MX). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). <b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ENCAPSULATED PERFUME PARTICLES AND DETERGENT COMPOSITIONS CONTAINING SAID PARTICLES <b>(57) Abstract</b> <p>Modified starch encapsulated High Impact Accord ("HIA") perfume particles. The particles consisting of a modified starch and perfume oil encapsulated by the starch and comprised of at least two HIA perfume ingredients which have a boiling point at 760 mm Hg, of 275 °C or lower, a calculated CLogP of 2.0 or higher, and an odor detection threshold less than or equal to 50 parts per billion (ppb). The encapsulated perfume particles are useful in laundry compositions.</p>		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## ENCAPSULATED PERFUME PARTICLES & DETERGENT COMPOSITIONS CONTAINING SAID PARTICLES

### FIELD OF THE INVENTION

The present invention relates to encapsulated perfume particles, especially for delivery of high impact accord (HIA) perfume ingredients, and detergent compositions comprising these encapsulated perfume particles, especially granular detergents.

### BACKGROUND OF THE INVENTION

Most consumers have come to expect scented detergent products and to expect that fabrics and other items which have been laundered with these products also have a pleasing fragrance. In many parts of the world handwashing is the predominant means of laundering fabrics. When handwashing soiled fabrics the user often comes in contact with the wash solution and is in close proximity to the detergent product used therein. Handwash solutions may also develop an offensive odor upon addition of soiled clothes. Therefore, it is desirable and commercially beneficial to add perfume materials to such products. Perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carryover from an aqueous laundry bath onto fabrics is often marginal. Industry, therefore, has long searched for an effective perfume delivery system for use in detergent products which provides long-lasting, storage-stable fragrance to the product, as well as fragrance which masks wet solution odor during use and provides fragrance to the laundered items.

Detergent compositions which contain perfume mixed with or sprayed onto the compositions are well known from commercial practice. Because perfumes are made of a combination of volatile compounds, perfume can be continuously emitted from simple solutions and dry mixes to which the perfume has been added. Various techniques have been developed to hinder or delay the release of perfume from compositions so that they will remain aesthetically pleasing for a longer length of time. To date, however, few of the methods deliver significant fabric and wet solution odor benefits after prolonged storage of the product.

Moreover, there has been a continuing search for methods and compositions which will effectively and efficiently deliver perfume into an aqueous laundry bath providing a relatively strong scent in the headspace just above the solution, then from the laundry bath onto fabric surfaces. Various methods of perfume delivery have been developed involving protection of the perfume through the wash cycle, with subsequent release of the perfume onto fabrics.

One method for delivery of perfume in the wash cycle involves combining the perfume with an emulsifier and water-soluble polymer, forming the mixture into particles, and adding

them to a laundry composition, as is described in U.S. Pat. 4,209,417, Whyte, issued June 24, 1980; U.S. Pat. 4,339,356, Whyte, issued July 13, 1982; and U.S. Pat. No. 3,576,760, Gould et al, issued April 27, 1971. However, even with the substantial work done by industry in this area, a need still exists for a simple, more efficient and effective perfume delivery system which can be mixed with laundry compositions to provide initial and lasting perfume benefits to fabrics which have been treated with the laundry product.

Another problem in providing perfumed products is the odor intensity associated with the products, especially high density granular detergent compositions. As the density and concentration of the detergent composition increase, the odor from the perfume components can become undesirably intense. A need therefore exists for a perfume delivery system which substantially releases the perfume odor during use and thereafter from the dry fabric, but which does not provide an overly- intensive odor to the product itself.

By the present invention it has now been discovered that perfume ingredients, can be selected based on specific selection criteria to maximize impact during and/or after the wash process, while minimizing the amount of ingredients needed in total to achieve a consumer noticeable benefit. Such compositions are desirable not only for their consumer noticeable benefits (e.g., odor aesthetics), but also for their potentially reduced cost through efficient use of lesser amounts of ingredients.

The present invention solves the long-standing need for a simple, effective, storage-stable delivery system which provides surprising odor benefits (especially wet solution odor benefits) during and after the laundering process. Further, encapsulated perfume-containing compositions have reduced product odor during storage of the composition.

#### SUMMARY OF THE INVENTION

The present invention relates to modified starch encapsulated High Impact Accord ("HIA") perfume particles; said particles comprising a modified starch and HIA perfume oil comprised of at least two HIA perfume ingredients which have a boiling point at 760 mm Hg, of 275°C or lower, a calculated CLogP of 2.0 or higher, and an odor detection threshold less than or equal to 50 parts per billion (ppb), wherein the perfume ingredients are encapsulated with the modified starch.

The present invention further relates to laundry compositions comprising from about 0.01% to 50% (preferably from about 0.05% to 8.0%; more preferably from about 0.05% to 3.0% and most preferably from about 0.05 to 1.0%) of a perfume particle according to the present invention and in total from about 50% to about 99.99% preferably from about 92% to 99.95%; more preferably from about 97% to 99.95% and most preferably from about 99% to 99.95%) of conventional laundry ingredients selected from the group consisting of surfactants,

builders, bleaching agents, enzymes, soil release polymers, dye transfer inhibitors, fillers and mixtures thereof.

All percentages, ratios, and proportions herein are on a weight basis unless otherwise indicated. All documents cited are hereby incorporated by reference in their entirety.

#### **DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides perfumed, dry particulate detergent compositions useful for the washing of fabrics having an especially desirable and noticeable odor attributable to a modified starch encapsulated HIA perfume particle. The HIA perfume oil contains at least two HIA perfume ingredients. An HIA perfume ingredient has a boiling point at 760 mm Hg, of 275°C or lower, a calculated  $\log_{10}$  of its octanol/water partition coefficient, P, of about 2 or higher and an odor detection threshold less than or equal to 50 ppb.

The HIA perfume ingredients are selected according to specific selection criteria described in detail hereinafter. The selection criteria further allow the formulator to take advantage of interactions between these agents when incorporated into the modified starch encapsulate to maximize consumer noticeable benefits while minimizing the quantities of ingredients utilized.

It is also preferable to use both free perfume and encapsulated perfume in the same particulate detergent composition, with the two perfumes being either the same, or two different perfumes. Normally, the free perfume provides the product (or container) perfume fragrance, and covers any base product odor, while the encapsulated perfume provides the in-use perfume odor when the detergent composition is diluted into the wash water.

#### **HIA Perfume Oil**

The HIA perfume oil comprises HIA perfume ingredients. An HIA perfume ingredient is characterized by its boiling point (B.P.), its octanol/water partition coefficient (P) and its odor detection threshold ("ODT"). The octanol/water partition coefficient of a perfume ingredient is the ratio between its equilibrium concentrations in octanol and in water. An HIA perfume ingredient of this invention has a B.P., determined at the normal, standard pressure of about 760 mm Hg, of about 275°C or lower, an octanol/water partition coefficient P of about 2,000 or higher, and an ODT of less than or equal to 50 parts per billion (ppb). Since the partition coefficients of the preferred perfume ingredients of this invention have high values, they are more conveniently given in the form of their logarithm to the base 10,  $\log P$ . Thus the preferred perfume ingredients of this invention have  $\log P$  of about 2 and higher.

The boiling points of many perfume ingredients, at standard 760 mm Hg are given in, e.g., "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, incorporated herein by reference.

The logP values of many perfume ingredients have been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, California, contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are preferably used instead of the experimental logP values in the selection of perfume ingredients which are useful in the present invention.

Odor detection thresholds are determined using a gas chromatograph. The gas chromatograph is calibrated to determine the exact volume of material injected by the syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 12 seconds, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine whether a material has a threshold below 50 ppb, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average across all panelists determines the threshold of noticeability.

The necessary amount of analyte is injected onto the column to achieve a 50 ppb concentration at the detector. Typical gas chromatograph parameters for determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector

7673 Autosampler

Column: J&W Scientific DB-1

Length 30 meters ID 0.25 mm film thickness 1 micron

Method:

Split Injection: 17/1 split ratio

Autosampler: 1.13 microliters per injection

Column Flow: 1.10 mL/minute

Air Flow: 345 mL/minute  
 Inlet Temp. 245°C  
 Detector Temp. 285°C  
 Temperature Information  
 Initial Temperature: 50°C  
 Rate: 5C/minute  
 Final Temperature: 280°C  
 Final Time: 6 minutes  
 Leading assumptions: (i) 12 seconds per sniff  
 (ii) GC air adds to sample dilution

An HIA perfume oil is composed of at least two HIA perfume ingredients, each HIA perfume ingredient having:

- (1) a standard B.P. of about 275°C or lower at 760 mm Hg, and;
- (2) a ClogP, or an experimental logP, of about 2 or higher, and;
- (3) an ODT of less than or equal to 50ppb and greater than 10 ppb,

and is encapsulated in a modified starch as described hereinafter, and used in a particulate detergent cleaning composition. The HIA perfume oil is very effusive and very noticeable when the product is in use as well as on fabric items that come in contact with the wash solution. Of the perfume ingredients in a given perfume oil, at least 40%, preferably at least 50% and most preferably at least 70% are HIA perfume ingredients.

Table 1 gives some non-limiting examples of HIA perfume ingredients.

**Table 1. HIA Perfume Ingredients**  
**HIA Ingredient**

4-(2,2,6-Trimethylcyclohex-1-enyl)-2-en-4-one  
 2,4 - Decadienoic acid, ethyl ester (E,Z) -  
 6-(and -8) isopropylquinoline  
 Acetaldehyde phenylethyl propyl acetal  
 Acetic acid, (2-methylbutoxy)-, 2-propenyl ester  
 Acetic acid, (3-methylbutoxy)-, 2-propenyl ester  
 2,6,10-Trimethyl-9-undecenal  
 Glycolic acid, 2-pentyloxy-, allyl ester  
 Hexanoic acid, 2-propenyl ester  
 1-Octen-3-ol  
 trans-Anethole  
 iso buthyl (z)-2-methyl-2-butenate  
 Anisaldehyde diethyl acetal  
 Benzenepropanal, 4-(1,1-dimethylethyl)-  
 2,6 - Nonadien-1-ol  
 3-methyl-5-propyl-cyclohexen-1-one  
 Butanoic acid, 2-methyl-, 3-hexenyl ester, (Z)-

Acetaldehyde, [(3,7-dimethyl-6-octenyl)oxy]-  
Lauroitrile  
2,4-dimethyl-3-cyclohexene-1-carbaldehyde  
2-Buten-1-one, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-  
2-Buten-1-one, 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-, (E)-  
gamma-Decalactone  
trans-4-decenal  
decanal  
2-Pentylcyclopentanone  
1-(2,6,6 Trimethyl 3 Cyclohexen-1-yl)-2 Buten-1-one)  
2,6-dimethylheptan-2-ol  
Benzene, 1,1'-oxybis-  
4-Penten-1-one, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-  
Butanoic acid, 2-methyl-, ethyl ester  
Ethyl anthranilate  
2-Oxabicyclo[2.2.2]octane, 1,3,3-trimethyl-  
Eugenol  
3-(3-isopropylphenyl)butanal  
methyl 2-octynoate  
4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one  
Pyrazine, 2-methoxy-3-(2-methylpropyl)-  
Quiniline, 6-secondary buty  
Iseugenol  
2H-Pyran-2-one, tetrahydro-6-(3-pentenyl)-  
Cis-3-Hexenyl Methyl Carbonate  
Linalool  
1,6,10-Dodecatriene, 7,11-dimethyl-3-methylene-, (E)-  
2,6-dimethyl-5-heptenal  
4,7 Methanoindan 1-carboxaldehyde, hexahydro  
2-methylundecanal  
methyl 2-nonynonate  
1,1-dimethoxy-2,2,5-trimethyl-4-hexene  
Benzoic acid, 2-hydroxy-, methyl ester  
4-Penten-1-one, 1-(5,5-dimethyl-1-cyclohexen-1-yl)  
2H-Pyran, 3,6-dihydro-4 methyl-2-(2-methyl-1-propenyl)-  
2,6-Octadienenitrile, 3,7-dimethyl-, (Z)-  
2,6-nonadienal  
6-Nonenal, (Z)-  
nonanal  
octanal  
2-Nonenenitrile  
Acetic acid, 4-methylphenyl ester  
Gamma Undecalactone  
2-norpinene-2-propionaldehyde 6,6 dimethyl  
4-nonanolide  
9-decen-1-ol  
2H-Pyran, tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-  
5-methyl-3-heptanone oxime  
Octanal, 3,7-dimethyl-  
4-methyl-3-decen-5-ol  
10-Undecen-1-al  
Pyridine, 2-(1-ethylpropyl)-  
Spiro[furan-2(3H),5'-[4,7]methano[5H]indene], decahydro-



The following are non-limiting examples of suitable perfume oil compositions for use in the present invention:

**Example 1**

HIA Perfume Ingredient Trade Name	Conc. Wt. %	ODT	Boiling Point ° C	ClogP
Eugenol	5	<50 PPB	259	2.4
Lilial	15	<50 PPB	280	3.9
Linalool	25	<50 PPB	197	3.0
beta-Naphthyl methyl ether	5	<50 PPB	270	3.2
Anisic Aldehyde	10	<50 PPB	249	2.0
Flor Acetate	10	<50 PPB	265	2.4
Ionone Beta	10	<50 PPB	265	3.8
Rose Oxide	10	<50 PPB	201	2.9
Damascenone	5	<50 PPB	260	4.3
Cyclal C	5	<50 PPB	199	2.4
<b>Total</b>	<b>100</b>			

**Example 2**

HIA Perfume Ingredient Trade Name	Conc. Wt. %	ODT	Boiling Point ° C	ClogP
Cyclal C	10	<50 PPB	199	2.4
Damascone Alpha	5	<50 PPB	255	4.7
Rose Oxide	10	<50 PPB	201	2.9
Ionone Beta	25	<50 PPB	265	3.8
Cis-3-Hexenyl Salicylate	15	<50 PPB	271	4.84
Methyl Octine Carbonate	5	<50 PPB	219	3.1
Lilial	30	<50 PPB	280	3.9
<b>Total</b>	<b>100</b>			

**Example 3**

HIA Perfume Ingredient Trade Name	Conc. Wt. %	ODT	Boiling Point ° C	ClogP
Damascone Alpha	5	<50 PPB	255	4.7
Cyclal C	5	<50 PPB	199	2.4
Rose Oxide	10	<50 PPB	201	2.9
Ionone Beta	25	<50 PPB	265	3.8
Frutene	15	<50 PPB	275	2.9
Anisic Aldehyde	10	<50 PPB	249	2.0
Ethyl-2-methyl Butyrate	5	<50 PPB	129	2.1
Lilial	25	<50 PPB	280	3.9
<b>Total</b>	<b>100</b>			

### Encapsulating Material

The HIA perfume oils are encapsulated with a water soluble, modified starch to form the modified starch encapsulate. Encapsulation of the HIA perfume oils in the water soluble modified starch provides an enhanced fragrance signal during use, when used in detergent compositions.

Starches suitable for encapsulating the perfume oils of the present invention can be made from, raw starch, pregelatinized starch, modified starch derived from tubers, legumes, cereal and grains, for example corn starch, wheat starch, rice starch, waxy corn starch, oat starch, cassava starch, waxy barley, waxy rice starch, sweet rice starch, amioca, potato starch, tapioca starch, oat starch, cassava starch, and mixtures thereof.

Modified starches suitable for use as the encapsulating matrix in the present invention include, hydrolyzed starch, acid thinned starch, starch esters of long chain hydrocarbons, starch acetates, starch octenyl succinate, and mixtures thereof.

The term "hydrolyzed starch" refers to oligosaccharide-type materials that are typically obtained by acid and/or enzymatic hydrolysis of starches, preferably corn starch. Suitable hydrolyzed starches for inclusion in the present invention include maltodextrins and corn syrup solids. The hydrolyzed starches for inclusion with the mixture of starch esters have a Dextrose Equivalent (DE) values of from about 10 to about 36 DE. The DE value is a measure of the reducing equivalence of the hydrolyzed starch referenced to dextrose and expressed as a percent (on a dry basis). The higher the DE value, the more reducing sugars present. A method for determining DE values can be found in Standard Analytical Methods of the Member Companies of Corn Industries Research Foundation, 6th ed. Corn Refineries Association, Inc. Washington, DC 1980, D-52.

Starch esters having a degree of substitution in the range of from about 0.01% to about 10.0% may be used to encapsulate the perfume oils of the present invention. The hydrocarbon part of the modifying ester should be from a C<sub>5</sub> to C<sub>16</sub> carbon chain. Preferably, octenylsuccinate (OSAN) substituted waxy corn starches of various types such as 1) waxy starch: acid thinned and OSAN substituted, 2) blend of corn syrup solids: waxy starch, OSAN substituted, and dextrinized, 3) waxy starch: OSAN substituted and dextrinized, 4) blend of corn syrup solids or maltodextrins with waxy starch: acid thinned OSAN substituted, and then cooked and spray dried, 5) waxy starch: acid thinned and OSAN substituted then cooked and spray dried, and 6) the high and low viscosities of the above modifications (based on the level of acid treatment) can also be used in the present invention.

Modified starches having emulsifying and emulsion stabilizing capacity such as starch octenyl succinates have the ability to entrap the perfume oil droplets in the emulsion due to the hydrophobic character of the starch modifying agent. The perfume oils remain trapped in the

modified starch until dissolved in the wash solution, due to thermodynamic factors i.e., hydrophobic interactions and stabilization of the emulsion because of steric hindrance.

#### **Example 4. Manufacture of Modified Starch Encapsulated HIA Perfume Particles**

The following is a non-limiting example of a suitable process for manufacture of a modified starch encapsulated HIA perfume particle for use in detergent compositions according to the present invention.

1. 225 g of CAPSUL modified starch (National Starch & Chemical) is added to 450 g of water at 24°C.
2. The mixture is agitated at 600 RPM (turbine impeller 2 inches in diameter) for 20 minutes.
3. 75 g perfume oil is added near the vortex of the starch solution.
4. The emulsion formed is agitated for an additional 20 minutes (at 600 RPM).
5. Upon achieving a perfume droplet size of less than 15 microns, the emulsion is pumped to a spray drying tower and atomized through a spinning disk with co-current airflow for drying. The inlet air temperature is set at 205-210°C, the exit air temperature is stabilized at 98-103°C.
6. Dried particles of the starch encapsulated perfume oil are collected at the dryer outlet.

Analysis of the finished HIA perfume particle (all % based on weight):

Total Perfume Oil	24.56%
Encapsulated Oil	24.46%
Free/Surface Oil	0.10%
Starch	72.57%
Moisture	2.87%
Particle Size Distribution	
< 50 micrometers	16%
50-500 micrometers	83%
> 500 micrometers	1%

Other known methods of manufacturing the starch encapsulates of the present invention, include but are not limited to, fluid bed agglomeration, extrusion, cooling/crystallization methods and the use of phase transfer catalysts to promote interfacial polymerization.

When a detergent composition containing the encapsulated HIA perfume particles described herein is added to water the modified starch of the perfume particles begins to dissolve in the water. Not wishing to be bound by theory it is believed that the dissolving modified starch swells and an emulsion of perfume droplets, modified starch and water is formed, the modified starch being the emulsifier and emulsion stabilizer. After the emulsion is formed, the perfume oil begins to coalesce into larger droplets of perfume, which can migrate to either the surface of the solution or to the surface of fabrics in the wash solution due to the

relative density difference between the perfume droplets (mostly low density hydrophobic oils) and the wash water. When the droplets reach either interface, they spread out quickly along the surface or interface. The spreading of the perfume droplet at the wash surface increases the surface area from which the perfume oil can volatilize, thereby releasing larger amounts of the perfume into the headspace above the wash solution. This provides a surprisingly strong and consumer noticeable scent in the headspace above the wash solution. When an equal mass of HIA perfume oil is delivered in a granular detergent via HIA particles according to the present invention as opposed to being sprayed on or delivered via cyclodextrin capsules the mass of perfume present in the headspace above the wash solution is ten fold greater. This can be confirmed by collection of the headspace air, from which the delivered perfume is subsequently condensed and its mass determined using conventional gas chromatography. Furthermore, the interaction of the perfume droplets with wet fabrics in solution provides a surprisingly strong and consumer noticeable scent on wet and dry fabrics.

Encapsulation of the HIA perfume oils as described above allows for loading of larger amounts of perfume oil than if they were encapsulated in a native starch granule. Encapsulation of perfume oils using cyclodextrin is limited by the particle size of the guest molecule (perfume) and the cavity of the host (cyclodextrin). It is difficult to load more than about 20% perfume into a cyclodextrin particle. However, encapsulation with a starch that has been modified to have emulsion properties does not impose this limitation. Since the encapsulation in the present invention is achieved by entrapping perfume oil droplets of less than 15 microns, preferably less than 5 microns and most preferably less than 2.5 microns in size, within the modified starch matrix, while the matrix is being formed by removal of water from the emulsion, more perfume can be loaded based on the type, method and level of modification of the starch. In contrast, traditional cyclodextrin molecules trap the perfume oil completely inside their cavity thereby limiting the size and amount of the perfume oil encapsulated. Loads much greater than 20% are possible when encapsulating with the modified starches described by this invention.

Encapsulation of the volatile HIA perfume oils also minimizes depletion during storage and when the product container is opened. Further, HIA perfumes are generally only released when detergents containing the encapsulated particle are dissolved in the wash solution. Furthermore, the water soluble encapsulating matrix protects the perfume oil from chemical degradation caused in the neat product as well as in the wash solution, by the different surfactant systems or bleaches which are commonly present in the particulate detergent compositions of this invention.

Other suitable matrix materials and process details are disclosed in, e.g., U.S. Pat. No. 3,971,852, Brenner et al., Issued July 27, 1976, which is incorporated herein by reference.

Water soluble perfume microcapsules containing conventional, non-HIA perfume oils can be obtained commercially, e.g., as IN-CAP<sup>®</sup> from Polak's Frutal Works, Inc., Middletown, New York; and as Optilok System<sup>®</sup> encapsulated perfumes from Encapsulated Technology, Inc., Nyack, New York.

The detergent compositions herein comprise from about 0.01% to 50% of the above described modified starch encapsulated HIA perfume particle. More preferably, the detergent compositions herein comprise from about 0.05% to 8.0% of the HIA perfume particle, even more preferably from about 0.5% to 3.0%. Most preferably, the detergent compositions herein contain from about 0.05% to 1.0% of the encapsulated HIA perfume particle. The encapsulated perfume particles preferably have size of from about 1 micron to about 1000 microns, more preferably from about 50 microns to about 500 microns.

The encapsulated perfume particles are used in compositions with deterative ingredients, as follows.

#### Optional Deterative Adjuncts

As a preferred embodiment, the conventional detergent ingredients are selected from typical detergent composition components such as deterative surfactants and deterative builders. Optionally, the detergent ingredients can include one or more other deterative adjuncts or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Usual deterative adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. and in Great Britain Patent Application No. 9705617.0, Trinh et al., published September 24, 1997. Such adjuncts are included in detergent compositions at their conventional art-established levels of use, generally from 0% to about 80% of the detergent ingredients, preferably from about 0.5% to about 20% and can include color speckles, suds boosters, suds suppressors, antitarnish and/or anticorrosion agents, soil-suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, solvents, solubilizing agents, chelating agents, clay soil removal/anti-redeposition agents, polymeric dispersing agents, processing aids, fabric softening components, static control agents, bleaching agents, bleaching activators, bleach stabilizers, etc.

#### Granular Detergent Composition

The encapsulated perfume particles hereinbefore described can be used in both low density (below 550 grams/liter) and high density granular detergent compositions in which the density of the granule is at least 550 grams/liter or in a laundry detergent additive product. Such high density detergent compositions typically comprise from about 30% to about 90% of deterative surfactant.

Low density compositions can be prepared by standard spray- drying processes. Various means and equipment are available to prepare high density granular detergent compositions. Current commercial practice in the field employs spray-drying towers to manufacture granular laundry detergents which often have a density less than about 500 g/l. Accordingly, if spray drying is used as part of the overall process, the resulting spray-dried detergent particles must be further densified using the means and equipment described hereinafter. In the alternative, the formulator can eliminate spray-drying by using mixing, densifying and granulating equipment that is commercially available.

High speed mixer/densifiers can be used in the present process. For example, the device marketed under the trademark "Lodige CB30" Recycler comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. Other such apparatus includes the devices marketed under the trademark "Shugi Granulator" and under the trademark "Drais K-TTP 80". Equipment such as that marketed under the trademark "Lodige KM600 Mixer" can be used for further densification.

In one mode of operation, the compositions are prepared and densified by passage through two mixer and densifier machines operating in sequence. Thus, the desired compositional ingredients can be admixed and passed through a Lodige mixture using residence times of 0.1 to 1.0 minute then passed through a second Lodige mixer using residence times of 1 minute to 5 minutes.

In another mode, an aqueous slurry comprising the desired formulation ingredients is sprayed into a fluidized bed of particulate surfactants. The resulting particles can be further densified by passage through a Lodige apparatus, as noted above. The perfume delivery particles are admixed with the detergent composition in the Lodige apparatus.

The final density of the particles herein can be measured by a variety of simple techniques, which typically involve dispensing a quantity of the granular detergent into a container of known volume, measuring the weight of detergent and reporting the density in grams/liter.

Once the low or high density granular detergent "base" composition is prepared, the encapsulated perfume particles of this invention are added thereto by any suitable dry-mixing operation.

#### Deposition of Perfume onto Fabric Surfaces

The method of washing fabrics and depositing perfume thereto comprises contacting said fabrics with an aqueous wash liquor comprising at least about 100 ppm of conventional deterative ingredients described hereinabove, as well as at least about 0.1 ppm of the above-disclosed encapsulated perfume particles. Preferably, the aqueous liquor comprises

from about 500 ppm to about 20,000 ppm of the conventional detergent ingredients and from about 10 ppm to about 200 ppm of the encapsulated perfume particles.

The encapsulated perfume particles work under all wash conditions, but they are particularly useful for providing odor benefits to the wet laundry solution during use and on dried fabrics during their storage.

The following nonlimiting examples illustrate the parameters of and compositions employed within the invention. All percentages, parts and ratios are by weight unless otherwise indicated.

Examples 5-11

Components	5	6	7	8	9	10	11
LAS	21.6	18	25	5	0	18	22
AES	1.0	1.5	--	--	--	1.0	--
ADHQ	0.7	0.6	--	--	--	0.6	--
AE	-	0.4	0.5	--	--	-	0.9
Phosphate	22	13	21	2	--	22	21
Silicate	7.5	7.5	10	--	--	7.5	3.5
Carbonate	13	9	10	80	70	13	4.5
Zeolite	-	1.5	--	--	--	-	-
DTPA	0.9	0.9	--	--	--	0.9	-
SOKALAN®	1.0	0.9	--	--	--	1.0	-
PEI 1800 E <sub>7</sub>	--	--	--	--	--	-	-
CMC	0.6	0.35	--	--	--	0.60	0.25
SRA-1	0.2	0.2	--	--	--	0.2	-
Protease/amylase	0.36	0.54	0.3	--	--	0.36	0.5
Cellulase	0.07	0.07	--	--	--	0.07	0.1
Lipase	--	--	0.05	--	--	--	-
Perborate	4.10	1.35	--	4.0	--	2.25	-
NOBS	1.70	1.15	--	--	--	1.90	-
TEAD	0.6	--	--	--	--	0	-
ZPS	0.001 5	0.007	--	--	--	0.0015	-
Brighteners	0.2	0.04	0.15	--	--	0.2	0.03
Encapsulated HIA Perfume particle from Example 1	0.8	0.8	0.8	0.8	0.8	0.8	0.8

Moisture + spray- on perfume	6.0	5.6	8.9	6.0	5.9	6.0	6.0
Sulfate	balanc e	balanc e	balan ce	balanc e	balanc e	balance	Balanc e



What is claimed is:

1. An encapsulated perfume particle comprising:
  - (a) a water-soluble modified starch solid matrix;
  - (b) a perfume oil encapsulated by the solid matrix of the modified starch, comprising at least 40% by weight of at least 2 High Impact Accord ("HIA") perfume ingredients, each of said perfume ingredient having (1) a boiling point at 760 mm Hg, of 275°C or lower, (2) a calculated CLogP of 2.0 or higher, and (3) an odor detection threshold ("ODT") less than or equal to 50 ppb and greater than 10 ppb.
2. An encapsulated perfume particle according to claim 1, wherein the perfume oil comprises at least 50%, preferably at least 70% of said HIA perfume ingredients.
3. An encapsulated perfume particle according to Claim 1 or Claim 2 wherein the modified starch comprises a starch raw material that has been modified by treatment of the starch raw material with octenyl-succinic acid anhydride.
4. A granular detergent composition comprising:
  - I) from about 0.01% to about 50%, by weight, of an encapsulated perfume particle comprising:
    - (a) a water-soluble modified starch solid matrix;
    - (b) a perfume oil comprising at least 40% by weight of at least 2 High Impact Accord ("HIA") perfume ingredients, each said HIA perfume ingredient having (1) a boiling point at 760 mm Hg, of 275°C or lower, (2) a calculated CLogP of 2.0 or higher, and (3) an odor detection threshold ("ODT") less than or equal to 50 ppb and greater than 10 ppb and;
  - II) from about 50% to about 99.99%, of conventional laundry ingredients selected from the group consisting of surfactants, builders, bleaching agents, enzymes, soil release polymers, dye transfer inhibitors, fillers, and mixtures thereof.
5. A granular detergent composition according to Claim 4 wherein the composition comprises from about 0.05% to about 8.0%, preferably from about 0.05% to 3.0%, and more preferably from about 0.05% to 1.0% by weight, of the encapsulated perfume particle, wherein the perfume oil comprises at least 50%, preferably at least 70% of said HIA perfume ingredients and from about 92% to about 99.95%,

preferably from about 97% to about 99.95%, most preferably from about 99% to about 99.95% of said conventional laundry ingredients.

6. A detergent composition according to Claim 4 or Claim 5 wherein the modified starch used to encapsulate the perfume oil comprises a starch raw material that has been modified by treatment said starch raw material with octenyl-succinic acid anyhydride.
7. A detergent composition according to Claim 4 or Claim 5 further comprising a perfume sprayed onto the surface of said detergent composition.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 99/00687

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/50 C11D3/22 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D A61K D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 500 138 A (BACON DENNIS R ET AL) 19 March 1996 (1996-03-19) comparative perfume D ---	1,3-7
Y	US 5 354 559 A (MOREHOUSE ALPHA L) 11 October 1994 (1994-10-11) claims 1,5 examples column 1, line 11 - line 18 ---	1,3-7
Y	EP 0 684 301 A (PROCTER & GAMBLE) 29 November 1995 (1995-11-29) claims 1,10,11 examples page 2, line 1 - line 3 page 4, line 13 - page 5, line 35 --- -/--	1,3-7

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 July 1999

Date of mailing of the international search report

04/08/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Neys, P

# INTERNATIONAL SEARCH REPORT

In .tional Application No

PCT/IB 99/00687

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 06235 A (PROCTER & GAMBLE) 20 February 1997 (1997-02-20) claims 1,2 examples 1,2 ---	1,2
A	US 5 234 610 A (BENVEGNI FERNANDO ET AL) 10 August 1993 (1993-08-10) claims 1,5-7 column 28, line 12 - line 19 -----	1,2

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.	PCT/IB 99/00687
Revised	04
Publication date	

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5500138 A	19-03-1996	AU 3832195 A	15-05-1996
		BR 9509410 A	03-11-1998
		CN 1169157 A	31-12-1997
		CZ 9701164 A	12-11-1997
		EP 0787176 A	06-08-1997
		JP 10507793 T	28-07-1998
		WO 9612785 A	02-05-1996
US 5354559 A	11-10-1994	US 5720978 A	24-02-1998
		CA 2034639 A	30-11-1991
EP 0684301 A	29-11-1995	GB 2288813 A	01-11-1995
		CA 2146686 A	29-10-1995
WO 9706235 A	20-02-1997	BR 9609985 A	12-01-1999
		CA 2228966 A	20-02-1997
		EP 0843719 A	27-05-1998
US 5234610 A	10-08-1993	US 5102564 A	07-04-1992
		AT 127152 T	15-09-1995
		AT 124422 T	15-07-1995
		AU 642867 B	04-11-1993
		AU 5317490 A	18-10-1990
		CA 2013487 A,C	12-10-1990
		CN 1046574 A	31-10-1990
		DE 69020408 D	03-08-1995
		DE 69021920 D	05-10-1995
		DE 69021920 T	02-05-1996
		DK 392606 T	15-01-1996
		DK 392608 T	20-11-1995
		EP 0392606 A	17-10-1990
		EP 0392608 A	17-10-1990
		ES 2076290 T	01-11-1995
		ES 2073507 T	16-08-1995
		FI 101384 B	15-06-1998
		GR 3018074 T	29-02-1996
		JP 3019978 A	29-01-1991
		MX 171691 B	10-11-1993
		PT 93730 A,B	20-11-1990
		PT 93758 A,B	20-11-1990